

# Re-examination of orbital ordering in $\text{LaMnO}_3$ : Electron-electron and electron-lattice interactions

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The interactions between  $e_g$  orbitals in neighboring sites are investigated in  $\text{LaMnO}_3$  by taking into account virtual exchange of electrons and phonons. The spin and orbital ordering temperatures and the spin wave dispersion relation are calculated. We find that the orbital ordering is mainly caused by the electronic interactions and that the Jahn-Teller coupling is much smaller than that reported previously. We propose that the elastic constant shows a characteristic change at the Néel temperature by the spin and orbital coupling and the higher-order Jahn-Teller coupling.

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## I. INTRODUCTION

In some classes of transition metal oxides, degeneracy of the  $d$  orbitals of a transition metal ion remains and electrons have a degree of freedom indicating the occupied orbital. This is called orbital degree of freedom.<sup>1</sup> For the colossal magnetoresistance (CMR) observed in perovskite manganese oxides,<sup>2-4</sup> the orbital degree of freedom is considered to play an important role, because the gigantic decrease of resistivity is observed in the vicinity of the transition from charge and orbital ordered phase to ferromagnetic metallic one. A parent compound of the CMR manganites,  $\text{LaMnO}_3$ , shows the orbital ordering below 780 K associated with the distortion of a  $\text{MnO}_6$  octahedron. It has been experimentally confirmed that the type of the orbital ordering is of  $C$ -type<sup>5</sup> where two kinds of orbitals are alternately aligned in the  $xy$  plane and the planes are stacked along the  $z$  axis. In addition to the orbital ordering, the so-called  $A$ -type antiferromagnetic (AF) ordering appears below 145 K, where spins are aligned parallel (antiparallel) in the  $xy$  plane ( $z$  axis).<sup>6,7</sup> It is well recognized that this anisotropic magnetic ordering is stabilized by the orbital ordering.<sup>5-15</sup>

In  $3d$  transition metal compounds with orbital degeneracy, two kinds of mechanisms have been proposed for the orbital ordering. One is caused by the superexchange (SE)-type interaction between orbitals in different sites. This interaction originates from the virtual exchange of electrons under the strong on-site electron-electron interactions.<sup>10,12</sup> Another mechanism of the orbital ordering is based on the cooperative Jahn-Teller (JT) effects where the lattice distortion occurs cooperatively and lifts the orbital degeneracy in the transition metal ions.<sup>16-19</sup> The effective interaction between orbitals in this mechanism is caused by virtual exchange of phonons. However, it is usually difficult to separate

contributions of these two mechanisms to the orbital ordering. This is because the two mechanisms provide the effective orbital interactions cooperatively.<sup>20-22</sup>

It has been supposed that the strong electron-lattice interaction exists and is necessary to explain CMR. The orbital ordering in  $\text{LaMnO}_3$  was also studied based on the cooperative JT effects.<sup>16,18,19</sup> The energy splitting of the two  $e_g$  orbitals due to the lattice distortion termed the JT energy ( $E_{JT}$ ) was estimated to be of the order of 1 eV by analyzing the orbital ordering temperature,<sup>18</sup> optical spectra<sup>23-28</sup> and the energy band calculation.<sup>29-31</sup> We note that in these analyses, the electron correlation effect was not taken into account properly. Actually, the on-site Coulomb interaction between electrons was estimated experimentally to be about 7 eV which is much larger than  $E_{JT}$ .<sup>32</sup> Therefore, it is necessary to re-examine the orbital ordering in  $\text{LaMnO}_3$  by considering both the cooperative JT effect and the SE interaction under the strong electron correlation on an equal footing.

In this paper, we investigate the interactions between  $e_g$  orbitals in neighboring sites originating from the electron-electron and electron-lattice interactions in  $\text{LaMnO}_3$ . Magnitudes of these interactions are determined through the calculation of the spin and orbital ordering temperatures and the spin stiffness constants. It is shown that  $E_{JT}$  is much smaller than that in the literature<sup>18,23-31</sup> and the orbital ordering is mainly caused by the electronic interactions. We find that the elastic constant shows a characteristic change at the Néel temperature by which the coupling constant of the higher-order JT effect is estimated.

In Sec. II, the model Hamiltonian which describes the orbital interactions caused by exchanges of electrons and phonons is derived. In Sec. III, we introduce the mean field approximation in the formulation of the orbital and spin ordering temperatures. In Sec. IV, by comparing the theoretical results of the ordering temperatures and

the spin stiffness constants with the experimental values, the magnitudes of the orbital interactions are determined numerically. Temperature dependence of the elastic constants are studied in Sec. V. The last section is devoted to the summary and discussion.

## II. MODEL

We start with the following Hamiltonian which includes spin, orbital and lattice degrees of freedom:

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{e-latt} + \mathcal{H}_{latt} + \mathcal{H}_{str} + \mathcal{H}_{e-str} + \mathcal{H}_{hiJT}. \quad (1)$$

$\mathcal{H}_e$  describes the electronic interactions and consists of three terms as

$$\mathcal{H}_e = \mathcal{H}_J + \mathcal{H}_H + \mathcal{H}_{AF}. \quad (2)$$

$\mathcal{H}_J$  represents the SE interaction between nearest neighboring (NN)  $e_g$  electrons derived from the generalized Hubbard model with orbital degeneracy<sup>12</sup> as

$$\begin{aligned} \mathcal{H}_J = & -2J_1 \sum_{\langle ij \rangle} \left( \frac{3}{4} n_i n_j + \vec{S}_i \cdot \vec{S}_j \right) \left( \frac{1}{4} - \tau_i^l \tau_j^l \right) \\ & - 2J_2 \sum_{\langle ij \rangle} \left( \frac{1}{4} n_i n_j - \vec{S}_i \cdot \vec{S}_j \right) \left( \frac{3}{4} + \tau_i^l \tau_j^l + \tau_i^l + \tau_j^l \right), \end{aligned} \quad (3)$$

where  $J_1 = t_0^2/(U' - I)$  and  $J_2 = t_0^2/(U' + I + 2J_H)$ .  $U, U'$  and  $I$  are the intra-, inter-orbital Coulomb interactions and the exchange interaction for  $e_g$  electrons, respectively, and a relation  $U = U' + I$  is assumed.  $J_H$  is the Hund coupling between  $e_g$  electron and  $t_{2g}$  spin  $\vec{S}_i^t$  ( $S^t = 3/2$ ), and  $t_0$  is the transfer intensity between NN  $d_{3z^2-r^2}$  orbitals along the  $z$  axis. Energy splitting between two  $e_g$  orbitals due to the JT effect is neglected in the denominators of  $J_1$  and  $J_2$ , because this splitting is much smaller than the Coulomb interactions.<sup>18,23-32</sup>  $\vec{S}_i$  is the spin operator of an  $e_g$  electron with  $S = 1/2$ .  $\tau_i^l$  is defined as  $\tau_i^l = \cos(\frac{2\pi}{3} m_l) T_{iz} - \sin(\frac{2\pi}{3} m_l) T_{ix}$  with  $(m_x, m_y, m_z) = (1, -1, 0)$  where  $l$  denotes a direction of a bond connecting sites  $i$  and  $j$ .  $\vec{T}_i$  is the pseudospin operator for the orbital degree of freedom, and  $\langle T_{iz} \rangle = +(-)1/2$  corresponds to the state where the  $d_{3z^2-r^2}$  ( $d_{x^2-y^2}$ ) orbital is occupied by an electron. The second and third terms in Eq. (2) describe the Hund coupling between  $e_g$  and  $t_{2g}$  spins and the AF SE interaction ( $J_{AF}$ ) between NN  $t_{2g}$  spins, respectively. These are given by

$$\mathcal{H}_H + \mathcal{H}_{AF} = -J_H \sum_i \vec{S}_i \cdot \vec{S}_i^t + J_{AF} \sum_{\langle ij \rangle} \vec{S}_i^t \cdot \vec{S}_j^t. \quad (4)$$

The second and third terms in Eq. (1) describe the electron-lattice interaction and the lattice dynamics, respectively. Here, we consider the displacement of O ions

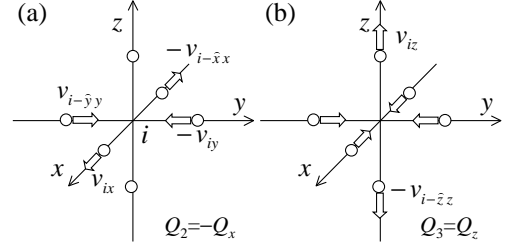


FIG. 1. The modes of the distortion of a  $\text{MnO}_6$  octahedron. (a)  $Q_2$  and (b)  $Q_3$  modes.

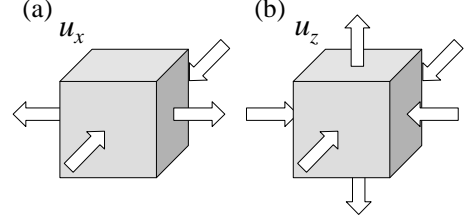


FIG. 2. The modes of the bulk strain. (a)  $u_x$  and (b)  $u_z$  modes.

along the direction connecting NN Mn ions, since the motion of O ions along the other directions does not couple linearly with the  $e_g$  orbitals. Thus,  $\mathcal{H}_{e-latt}$  is given by

$$\mathcal{H}_{e-latt} = -g_{JT} \sum_{i,l=x,z} Q_{il} T_{il}, \quad (5)$$

where  $g_{JT}$  is the coupling constant.  $Q_{ix}$  and  $Q_{iz}$  are the normal modes of the lattice distortion at site  $i$  given by  $Q_{ix} = \frac{1}{\sqrt{2}}(-v_{ix} + v_{i-\hat{x}x} + v_{iy} - v_{i-\hat{y}y})$  and  $Q_{iz} = \frac{1}{\sqrt{6}}(2v_{iz} - 2v_{i-\hat{z}z} - v_{ix} + v_{i-\hat{x}x} - v_{iy} + v_{i-\hat{y}y})$ .<sup>16</sup>  $v_{i\xi}$  is the displacement of an O ion at  $\vec{r}_i + \frac{a}{2}\hat{\xi}$  and  $a$  is the lattice constant. These normal modes are schematically shown in Fig. 1. The third term in Eq. (1),  $\mathcal{H}_{latt}$ , is given by

$$\mathcal{H}_{latt} = \sum_{\vec{k}, \xi=x,y,z} \frac{\hbar \omega_{\vec{k}}}{2} (p_{\vec{k}\xi}^* p_{\vec{k}\xi} + q_{\vec{k}\xi}^* q_{\vec{k}\xi}), \quad (6)$$

where  $q_{\vec{k}\xi}$  is the normal coordinate of lattice vibration with direction of displacement  $\xi$  and momentum  $\vec{k}$ , and  $p_{\vec{k}\xi}$  is the canonical conjugate momentum of  $q_{\vec{k}\xi}$ .  $q_{\vec{k}\xi}$  and  $p_{\vec{k}\xi}$  satisfy the relation  $v_{i\xi} = \frac{1}{\sqrt{N}} \sum_i e^{i\vec{k}\cdot\vec{r}_i} \sqrt{\frac{\hbar}{m\omega_{\vec{k}}}} q_{\vec{k}\xi}$  with  $N$  being the total number of Mn sites. The frequency of the lattice vibration is independent of  $\vec{k}$  and is given by  $\omega_{\vec{k}} = \sqrt{\frac{K}{m}}$  with  $m$  being the mass of an O ion, since only the spring constant  $K/2$  between NN Mn and O ions is taken into account.  $\mathcal{H}_{str}$  and  $\mathcal{H}_{e-str}$  in Eq. (1) describe the elastic energy and electron-strain coupling, respectively,<sup>17</sup> as

$$\mathcal{H}_{str} = \frac{Vc_0}{2} (u_x^2 + u_z^2), \quad (7)$$

and

$$\mathcal{H}_{e-str} = -2g_0 \sqrt{\frac{Vc_0}{N}} \sum_i (u_x T_{ix} + u_z T_{iz}). \quad (8)$$

Here,  $V$  is the volume of the system and  $c_0$  is the elastic constant. The electron-strain coupling constant  $g_0$  is related to  $g_{JT}$  as  $g_0 = \frac{a}{2} \sqrt{\frac{N}{Vc_0}} g_{JT}$ . The bulk distortions  $u_x$  and  $u_z$  are represented by the elastic strain  $e_{\rho\rho'}(\rho, \rho' = x, y, z)$  as  $u_x = \frac{1}{\sqrt{2}}(e_{yy} - e_{xx})$  and  $u_z = \frac{1}{\sqrt{6}}(2e_{zz} - e_{yy} - e_{xx})$ , respectively.<sup>17</sup> Schematic pictures of the bulk distortions are presented in Fig. 2. The last term of Eq. (1) describes the higher-order JT coupling given by

$$\mathcal{H}_{hiJT} = -B \frac{Vc_0}{g_0^2 N} \sum_i \left\{ (Q_{iz}^2 - Q_{ix}^2) T_{iz} - 2Q_{iz} Q_{ix} T_{ix} \right\}, \quad (9)$$

with coupling constant  $B$ .

Now, we derive the effective Hamiltonian describing the inter-site orbital interaction through the exchange of phonon<sup>17</sup> from  $\mathcal{H}_{e-latt}$  and  $\mathcal{H}_{latt}$ .  $\mathcal{H}_{e-latt}$  is rewritten by using the Fourier transforms of  $q_{\vec{k}\xi} = \frac{1}{\sqrt{N}} \sum_i e^{-i\vec{k}\vec{r}_i} q_{i\xi}$  and  $T_{\vec{k}l} = \frac{1}{\sqrt{N}} \sum_i e^{-i\vec{k}\vec{r}_i} T_{il}$  as

$$\mathcal{H}_{e-latt} = -2 \sum_{\substack{\vec{k} \ l=x,z \\ \xi=x,y,z}} \sqrt{\hbar\omega_{\vec{k}}} g_{\vec{k}\xi l} T_{-\vec{k}l} q_{\vec{k}\xi}. \quad (10)$$

Here,  $g_{\vec{k}\xi l}$  is defined as

$$g_{\vec{k}\xi l} = \frac{1}{2} \frac{g_{JT}}{\sqrt{K}} (1 - e^{-ik_\xi a}) C_{l\xi}, \quad (11)$$

with

$$C_{l\xi} = \begin{pmatrix} \frac{1}{\sqrt{2}}, & -\frac{1}{\sqrt{2}}, & 0 \\ -\frac{1}{\sqrt{6}}, & -\frac{1}{\sqrt{6}}, & \frac{2}{\sqrt{6}} \end{pmatrix}_{l\xi}. \quad (12)$$

Then, by using the canonical transformation, the linear couplings between  $e_g$  electrons and lattice distortion are eliminated as

$$\begin{aligned} \mathcal{H}_{e-latt} + \mathcal{H}_{latt} = & -\frac{g_{JT}^2}{K} \sum_{\vec{k}ll'} \tilde{A}_{\vec{k}ll'} T_{-\vec{k}l} T_{\vec{k}l'} \\ & + \sum_{i\xi} \frac{\hbar\omega_{\vec{k}}}{2} (\tilde{p}_{\vec{k}\xi}^2 + \tilde{q}_{\vec{k}\xi}^2), \end{aligned} \quad (13)$$

where

$$\tilde{A}_{\vec{k}ll'} = \frac{1}{2} \begin{pmatrix} 2 - c_x - c_y, & \frac{1}{\sqrt{3}}(c_x - c_y) \\ \frac{1}{\sqrt{3}}(c_x - c_y), & \frac{1}{3}(6 - c_x - c_y - 4c_z) \end{pmatrix}_{ll'}, \quad (14)$$

and  $c_\rho = \cos k_\rho a$ .  $\tilde{q}_{\vec{k}\xi}$  is the new phonon coordinate given by

$$\tilde{q}_{\vec{k}\xi} = q_{\vec{k}\xi} - \frac{2}{\sqrt{\hbar\omega_{\vec{k}}}} \sum_l g_{\vec{k}\xi l}^* T_{-\vec{k}l}, \quad (15)$$

and  $\tilde{p}_{\vec{k}\xi}$  is the canonical conjugate momentum for  $\tilde{q}_{\vec{k}\xi}$ . The first and second terms of the right hand side in Eq. (13) are denoted by  $\tilde{\mathcal{H}}_{o-o}$  and  $\tilde{\mathcal{H}}_{latt}$ , respectively. Here, we neglect the noncommutability between  $\mathcal{H}$  (Eq. (1)) and  $\tilde{q}_{\vec{k}\xi}$ .  $\tilde{\mathcal{H}}_{o-o}$  includes the self-interaction of orbital, which does not contribute to the orbital order-disorder transition. Therefore, by subtracting this term, we obtain the following form:

$$\mathcal{H}_{o-o} = -\frac{g_{JT}^2}{K} \sum_{\vec{k}ll'} A_{\vec{k}ll'} T_{-\vec{k}l} T_{\vec{k}l'}, \quad (16)$$

with

$$A_{\vec{k}ll'} = \frac{1}{2} \begin{pmatrix} -c_x - c_y, & \frac{1}{\sqrt{3}}(c_x - c_y) \\ \frac{1}{\sqrt{3}}(c_x - c_y), & \frac{1}{3}(-c_x - c_y - 4c_z) \end{pmatrix}_{ll'}. \quad (17)$$

Then, we obtain the effective Hamiltonian for the spin, orbital and lattice degrees of freedom in LaMnO<sub>3</sub> given by

$$\mathcal{H}_{eff} = \mathcal{H}_e + \tilde{\mathcal{H}}_{latt} + \mathcal{H}_{o-o} + \mathcal{H}_{e-str} + \mathcal{H}_{str} + \mathcal{H}_{hiJT}. \quad (18)$$

### III. MEAN FIELD APPROXIMATION

In order to calculate the orbital ordering temperature from Eq. (18), we introduce the mean field approximation at finite temperatures. It is experimentally confirmed that the orbital order-disorder transition in LaMnO<sub>3</sub> is of the first order but is close to the second order transition; a discontinuity of the orbital order parameter at  $T_{OO}$  is negligible.<sup>5</sup> Therefore, we expect that the higher-order JT coupling, which brings about the first order phase transition, is much smaller than the linear JT coupling. Thus, we neglect  $\mathcal{H}_{hiJT}$  in Eq. (18) and calculate  $T_{OO}$ . We will consider  $\mathcal{H}_{hiJT}$  in the calculation of the elastic constant presented in Sec. V.

The  $A$ -type AF spin and  $C$ -type orbital orderings are observed in LaMnO<sub>3</sub>.<sup>5-7</sup> Two sublattices for the orbital (spin) ordering are denoted by  $A$  and  $B$  ( $a$  and  $b$ ) and the following mean fields are introduced:  $\langle S_{a,bz} \rangle$ ,  $\langle S_{a,bz}^t \rangle$ ,  $\langle T_{A,Bx} \rangle$  and  $\langle T_{A,Bz} \rangle$ . The free energy of the system is obtained in the mean field approximation as follows:

$$\begin{aligned} \mathcal{F}_0 = & \frac{Vc_0}{2} (u_x^2 + u_z^2) \\ & - \frac{N}{2} \left\{ 6J_{xy}^t \langle T_{Ax} \rangle \langle T_{Bx} \rangle + 2J_{xy}^t \langle T_{Az} \rangle \langle T_{Bz} \rangle \right. \\ & + 2J_z^t (\langle T_{Az} \rangle^2 + \langle T_{Bz} \rangle^2) \\ & + J_2 (2\langle S_{az} \rangle \langle S_{bz} \rangle - \langle S_{az} \rangle^2 - \langle S_{bz} \rangle^2) \\ & \left. \times (\langle T_{Az} \rangle + \langle T_{Bz} \rangle) \right\} \end{aligned}$$

$$\begin{aligned}
& + \frac{N}{2}(J_1 - 3J_2)(\langle S_{az} \rangle^2 + \langle S_{bz} \rangle^2 + \langle S_{az} \rangle \langle S_{bz} \rangle) \\
& - N J_{AF} (\langle S_{az}^t \rangle^2 + \langle S_{az}^t \rangle \langle S_{bz}^t \rangle + \langle S_{az}^t \rangle^2) \\
& - \frac{N}{2\beta} (\ln z_a^s + \ln z_b^s + \ln z_A^t + \ln z_B^t), \quad (19)
\end{aligned}$$

where  $\beta = 1/T$ .  $z_{a(b)}^s$  and  $z_{A(B)}^t$  in the last four terms represent the partition functions of spin and orbital given by  $z_{a(b)}^s = \text{Tr} \exp(-\beta \mathcal{H}_{a(b)}^s)$  and  $z_{A(B)}^t = \text{Tr} \exp(-\beta \mathcal{H}_{A(B)}^t)$ , respectively.  $\mathcal{H}_{a(b)}^s$  is the mean field Hamiltonian describing the spin state in sublattice  $a$  ( $b$ ) as

$$\mathcal{H}_{a(b)}^s = 4J_{xy}^s \langle \tilde{S}_{a(b)z} \rangle \tilde{S}_{a(b)z} + 2J_z^s \langle \tilde{S}_{b(a)z} \rangle \tilde{S}_{a(b)z}, \quad (20)$$

where  $J_{xy}^s$  and  $J_z^s$  represent the effective exchange interaction between NN spins in the  $xy$  plane and along the  $z$  direction, respectively. These are explicitly given by

$$\begin{aligned}
J_{xy}^s = & -\frac{1}{32}(J_1 - 3J_2) \\
& + \frac{1}{32}(J_1 + J_2)(3\langle T_{Ax} \rangle \langle T_{Bx} \rangle + \langle T_{Az} \rangle \langle T_{Bz} \rangle) \\
& - \frac{1}{16}J_2(\langle T_{Az} \rangle + \langle T_{Bz} \rangle) + \frac{9}{16}J_{AF}, \quad (21)
\end{aligned}$$

and

$$\begin{aligned}
J_z^s = & -\frac{1}{32}(J_1 - 3J_2) + \frac{1}{8}(J_1 + J_2)\langle T_{Az} \rangle^2 \\
& + \frac{1}{16}J_2(\langle T_{Az} \rangle + \langle T_{Bz} \rangle) + \frac{9}{16}J_{AF}. \quad (22)
\end{aligned}$$

In Eq. (20), we introduce a spin operator  $\tilde{S}_i$  with  $\tilde{S} = 2$ , rewrite  $\vec{S}_i$  and  $\vec{S}_i^t$  as  $\vec{S}_i = \frac{1}{4}\tilde{\vec{S}}_i$  and  $\vec{S}_i^t = \frac{3}{4}\tilde{\vec{S}}_i$ , respectively, and eliminate the largest energy parameter  $J_H$  in Eq. (18). Due to the A-AF spin structure, the relation  $\langle \tilde{S}_{az} \rangle = -\langle \tilde{S}_{bz} \rangle$  is satisfied.  $\mathcal{H}_{A(B)}^t$  is the mean field Hamiltonian describing the orbital state in sublattice  $A$  ( $B$ ) as

$$\begin{aligned}
\mathcal{H}_{A(B)}^t = & 6J_{xy}^t \langle T_{B(A)x} \rangle T_{A(B)x} + 2\tilde{J} T_{A(B)z} \\
& + (2J_{xy}^t \langle T_{B(A)z} \rangle + 4J_z^t \langle T_{A(B)z} \rangle) T_{A(B)z} \\
& - 2g_0 \sqrt{\frac{Vc_0}{N}} (u_x T_{A(B)x} + u_z T_{A(B)z}), \quad (23)
\end{aligned}$$

where  $J_{xy}^t$  and  $\tilde{J}$  are

$$J_{xy}^t = \frac{1}{4}(3J_1 - J_2) + (J_1 + J_2)\langle S_{iz} \rangle \langle S_{i+\hat{x}(i+\hat{z})} \rangle \quad (24)$$

and

$$\tilde{J} = 2J_2(\langle S_{az} \rangle^2 - \langle S_{az} \rangle \langle S_{bz} \rangle), \quad (25)$$

respectively. For the observed  $C$ -type orbital ordered state, we have the following conditions:  $\langle T_{Az} \rangle = \langle T_{Bz} \rangle$  and  $\langle T_{Ax} \rangle = -\langle T_{Bx} \rangle$ .

By minimizing the free energy  $\mathcal{F}_0$  with respect to  $\langle T_{Al} \rangle$  for  $l = x, z$  and  $\langle \tilde{S}_{az} \rangle$ , the following self-consistent equations are obtained:

$$\langle T_{Al} \rangle = \text{Tr} \left\{ T_{Al} \exp(-\beta \mathcal{H}_A^t) \right\} / z_A^t, \quad (26)$$

$$\langle \tilde{S}_{az} \rangle = \text{Tr} \left\{ \tilde{S}_{az} \exp(-\beta \mathcal{H}_a^s) \right\} / z_a^s. \quad (27)$$

Equations (26) and (27) are numerically solved under the conditions of  $u_z = 2g_0 \sqrt{N/Vc_0} \langle T_{Az} \rangle$  and  $u_x = 0$  which are derived from  $\partial \mathcal{F} / \partial u_x = 0$  and  $\partial \mathcal{F} / \partial u_z = 0$ , respectively.

#### IV. TRANSITION TEMPERATURES AND SPIN WAVE DISPERSION

Among several parameters in the Hamiltonian Eqs. (1) and (18), values of  $J_1, J_2$  and  $g_{JT}$  are determined by calculating the spin and orbital ordering temperatures and the spin wave dispersion relation. The other parameters are chosen to be  $J_{AF} = 1$ ,  $a^2 K = 17 \times 10^4$  and  $a^3 c_0 = 2 \times 10^4$  meV, which are derived from the Néel temperature in  $\text{CaMnO}_3$ ,<sup>6</sup> the phonon frequency determined by the infrared absorption spectra<sup>35</sup> and the elastic constant.<sup>36</sup> The lattice constant  $a$  and the static JT distortion  $Q (= \sqrt{Q_{iz}^2 + Q_{ix}^2})$  are chosen to be  $a = 4 \text{ \AA}$  and  $Q = 0.3 \text{ \AA}$ , respectively.<sup>37</sup>

Firstly, we calculate the transition temperatures. The orbital ordering temperature in the mean field approximation  $T_{OO}^{MF}$  is given by

$$T_{OO}^{MF} = \frac{1}{2} \left\{ \frac{3}{4}(3J_1 - J_2) + \frac{g_{JT}^2}{K} \right\}, \quad (28)$$

and the Néel temperature for the A-AF ordering  $T_N^{MF}$  is given by the solution of the following equation:

$$T_N^{MF} = -8J_{xy}^s + 4J_z^s, \quad (29)$$

where  $J_{xy}^s$  and  $J_z^s$  defined in Eqs. (21) and (22) are the functions of  $T_N^{MF}$ . By fitting  $T_{OO}^{MF}$  and  $T_N^{MF}$  to the experimental transition temperatures  $T_{OO} = 780 \text{ K}$  (Ref. 5) and  $T_N = 140 \text{ K}$  (Refs. 6 and 7), respectively,  $J_2$  and  $g_{JT}Q$  are calculated as functions of  $J_1$ . In general, the mean field approximation tends to overestimate the transition temperature. Therefore, we also estimate the parameter values of  $J_1, J_2$  and  $g_{JT}Q$  by considering the correction of the mean field transition temperatures. For the Néel temperature, we revise  $T_N^{MF}$  as  $bT_N^{MF}$  with  $b = 0.63$ , which is the ratio between  $T_N$  for the  $S = 1/2$  AF Heisenberg model obtained in the high-temperature expansion and that in the mean field approximation.<sup>38</sup> As for the orbital ordering temperature, we revise as  $aT_{OO}^{MF}$  with  $a = 0.75$ , which is obtained by the calculation of  $T_N$  for the  $S = 1/2$  AF Ising model.<sup>38</sup> This is because the orbital part of the Hamiltonian (Eq. (3)) has a discontinuous symmetry, although this symmetry is higher than that of the Ising model.

The spin stiffness constant provides another conditions for  $J_1$ ,  $J_2$  and  $g_{JT}$ . Although the JT distortion does not directly couple with the spin degree of freedom,  $g_{JT}$  modifies the orbital state and affects the SE interaction between NN spins. We calculate the spin wave dispersion at  $T = 0$  and compare it with the experimental one. Here, the orbital and lattice degrees of freedom are assumed to be frozen, since the energy scale of orbital excitations<sup>12,39</sup> and optical phonon are much larger than that of spin wave. Then, the relevant parts of the Hamiltonian in Eq. (1) are given by

$$\mathcal{H}_{SW} = \mathcal{H}_e + \mathcal{H}_{e-latt}. \quad (30)$$

The static distortion of a  $\text{MnO}_6$  octahedron is written as  $(Q_{iz}, Q_{ix}) = Q(\cos \theta_i^{JT}, \sin \theta_i^{JT})$  where  $\theta_A^{JT} = -\theta_B^{JT} = \frac{2\pi}{3}$ . The orbital ordered state is determined in the mean field approximation.<sup>33</sup> By applying the Holstein-Primakoff transformation to the spin operators, the dispersion relation of the spin wave is calculated. Experimentally, the spin wave in  $\text{LaMnO}_3$  was measured by the neutron scattering experiments in Refs. 11 and 34. The authors in these papers analyzed the experimental data by using the Heisenberg model with the NN SE interactions. They obtained magnitude of the interaction in the  $xy$  plane ( $J_{xy}^s$ ) and that in the  $z$  axis ( $J_z^s$ ), which are defined in Eqs. (21) and (22), as  $2J_{xy}^s = -3.34$  meV and  $2J_z^s = 2.42$  meV.

By fitting the theoretical results of the orbital ordering temperature, the Néel temperature for the  $A$ -AF ordering and the spin stiffness constant to the experimental values, we estimate  $J_1$ ,  $J_2$  and  $g_{JT}$ .  $J_2$  and  $g_{JT}Q$  are plotted as functions of  $J_1$  in Fig. 3 (a) and (b), respectively. Solid and broken curves are obtained from the transition temperatures,  $T_{OO}$  and  $T_N$ . The actual values of the parameters are expected to exist in the shaded regions. Dotted curves are obtained from the spin stiffness constants. The analyses for  $T_{OO}$  and  $T_N$  (solid and broken curves in Fig. 3 (a) and (b)) show that  $J_2$  increases and  $g_{JT}Q$  decreases with increasing  $J_1$ . This is because  $(3J_1 - J_2)$  and  $g_{JT}^2/K$  contribute cooperatively to  $T_{OO}$ , as shown in Eq. (28). On the other hand, the analyses for the spin stiffness constant (dotted curves in Fig. 3 (a) and (b)) show that both  $J_2$  and  $g_{JT}Q$  increase with increasing  $J_1$ , i.e.,  $J_1$  competes with both  $J_2$  and  $g_{JT}Q$ . This is attributed to the facts that (1)  $J_1$  and  $J_2$  are the ferromagnetic and antiferromagnetic interactions, respectively, and (2)  $g_{JT}Q$  favors the  $(d_{3x^2-r^2}/d_{3y^2-r^2})$ -type orbital ordered state where the ferromagnetic interaction in the  $xy$  plane caused by  $J_1$  is weaker than that without  $g_{JT}Q$ . The magnitudes of  $J_1$ ,  $J_2$  and  $g_{JT}Q$  are obtained from the intersection points of solid (broken) curve and dotted curve in Fig. 3 (a) and (b). We obtain  $J_1 = 75 \sim 85$  meV,  $J_2 = 25 \sim 40$  meV and  $E_{JT} = g_{JT}Q = 50 \sim 100$  meV. It is stressed that the value of  $E_{JT}$  is much smaller than that in the literature, i.e.,  $E_{JT} > 1$  eV.<sup>18,23-31</sup> In the case that  $a^2K = 17 \times 10^4$  meV, the coupling constant of the inter-site orbital interaction through the exchange of phonons

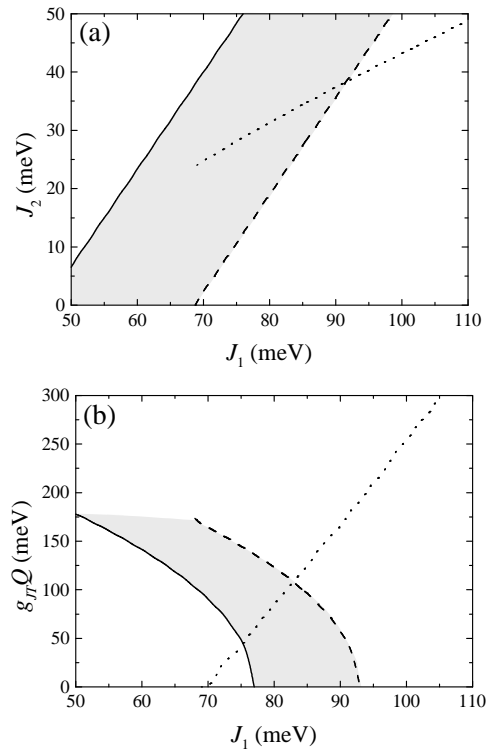


FIG. 3. (a)  $J_2$  and (b)  $g_{JT}Q$  as functions of  $J_1$ . Solid and broken curves are obtained from the analyses of transition temperatures  $T_{OO}$  and  $T_N$ . For broken curves, the correction from the mean field approximation is taken into account (see the text). The actual values of the parameters are expected to exist in the shaded regions. Dotted curves are obtained from the analysis of the spin stiffness constants. Other parameter values are chosen to be  $J_{AF} = 1$  meV,  $a^2K = 17 \times 10^4$  meV,  $B = 0$  meV,  $Q = 0.3$  Å and  $a = 4$  Å.

$g_{JT}^2/K$  is about  $3 \sim 10$  meV which is much smaller than  $J_1$ . We conclude that the small  $E_{JT}$  comes from the strong Coulomb interaction and the orbital ordering in  $\text{LaMnO}_3$  is dominated by the interaction through the virtual exchange of electrons. If  $J_1$  and  $J_2$  are neglected to estimate  $T_{OO}$ , we obtain  $E_{JT}$  to be  $400 \sim 700$  meV for  $a^2K = 17 \times 10^4$  meV<sup>35</sup> and  $600 \sim 1100$  meV for  $a^2K = 40 \times 10^4$  meV.<sup>18</sup> The latter value of  $E_{JT}$  is of the same order of magnitude given in Ref. 18.

## V. ELASTIC CONSTANTS

The elastic constants provide information of the higher-order JT coupling,<sup>17,19</sup> although the coupling constant  $B$  is supposed to be smaller than that in the linear JT coupling. In this section, we examine the elastic constants taking into account the electron-electron and electron-lattice interactions and the higher-order JT coupling.

We start with the model Hamiltonian in Eq. (18). The elastic constants are the coefficients of the  $\delta u_l^2$  terms in

the free energy, where  $\delta u_l$  is the deviation of strain  $u_l$  from that in the thermal equilibrium. Here, the deviations of  $T_{Al}$  and  $T_{Bl}$  from the thermal equilibrium,  $\delta T_{Al}$  and  $\delta T_{Bl}$ , are also introduced.  $\delta T_{Al}$  and  $\delta T_{Bl}$  are induced by an external strain  $\delta u_{l'}$  and the relations between them are derived later. Now, the free energy is expanded up to the second order of  $\delta T_{Al}$ ,  $\delta T_{Bl}$  and  $\delta u_l$  as

$$\begin{aligned} \mathcal{F} = & \tilde{\mathcal{F}}_0 + \frac{Vc_0}{2}(\delta u_x^2 + \delta u_z^2) \\ & - \frac{N}{2} \left[ 6J_{xy}^t \delta T_{Ax} \delta T_{Bx} + 2J_{xy}^t \delta T_{Az} \delta T_{Bz} \right. \\ & \quad \left. + 2J_z^t \{ (\delta T_{Az} + \delta T_{Bz})^2 - (\delta T_{Az} - \delta T_{Bz})^2 \} \right] \\ & - \frac{\beta N}{4} \left\{ F_{xx} (C_x^A + C_x^B) + F_{zz} (C_x^A + C_x^B) \right. \\ & \quad \left. + 2F_{xz} (C_x^A C_z^A - C_x^B C_z^B) \right\}. \end{aligned} \quad (31)$$

Here,  $\tilde{\mathcal{F}}_0$  is given by Eq. (19) where  $z_{A(B)}^t$  is replaced by  $z_{A(B)}^t = \text{Tr} \exp(-\beta \tilde{\mathcal{H}}_{A(B)}^t)$ ,  $\tilde{\mathcal{H}}_{A(B)}^t$  being given by

$$\begin{aligned} \tilde{\mathcal{H}}_{A(B)}^t = & \mathcal{H}_{A(B)}^t \\ & - B \frac{Vc_0}{Ng_0} \left\{ (Q_{A(B)z}^2 - Q_{A(B)x}^2) T_{A(B)z} \right. \\ & \quad \left. - 2Q_{A(B)z} Q_{A(B)x} T_{A(B)x} \right\}. \end{aligned} \quad (32)$$

The last term of this equation comes from the higher-order JT coupling. We assume that the equilibrium values of  $Q_{Al}$  appearing in this term are given by  $Q_{Az} = au_z$  and  $Q_{Ax} = 4\frac{g_{JT}}{K} \langle T_{Ax} \rangle$  by considering the definition of the strain  $u_z$  and the linear JT coupling in Eq. (5).  $C_l^\alpha$ 's are the coefficients of  $T_{\alpha l}$  in  $\mathcal{H}_\alpha^t$  (Eq. (23)) where  $\langle T_{Al} \rangle$ ,  $\langle T_{Bl} \rangle$  and  $u_l$  are replaced by  $\langle T_{Al} \rangle + \delta T_{Al}$ ,  $\langle T_{Bl} \rangle + \delta T_{Bl}$  and  $u_l + \delta u_l$ , respectively. Their explicit forms are given by

$$C_x^A = 6J_{xy}^t \delta T_{Bx} - 2g_0 \sqrt{\frac{Vc_0}{N}} \delta u_x, \quad (33)$$

$$C_z^A = 2J_{xy}^t \delta T_{Bz} + 4J_z^t \delta T_{Az} - 2g_0 \sqrt{\frac{Vc_0}{N}} \delta u_z, \quad (34)$$

$$C_x^B = 6J_{xy}^t \delta T_{Ax} - 2g_0 \sqrt{\frac{Vc_0}{N}} \delta u_x, \quad (35)$$

$$C_z^B = 2J_{xy}^t \delta T_{Az} + 4J_z^t \delta T_{Bz} - 2g_0 \sqrt{\frac{Vc_0}{N}} \delta u_z. \quad (36)$$

Here, the term originating from the higher-order JT coupling is neglected.<sup>17</sup>  $F_{ll'}$  in Eq. (31) represents the self-correlation function of the orbital given by

$$F_{ll'} = \langle T_{Al} \rangle \langle T_{Al'} \rangle - K_{ll'} \quad (37)$$

with

$$\begin{aligned} K_{ll'} = & \frac{1}{z_A^t} \left[ \sum_{mm'} e^{-\beta \varepsilon_m} \delta_{\varepsilon_m, \varepsilon_{m'}} - \frac{2}{\beta} \sum_{\substack{m > m' \\ (\varepsilon_m \neq \varepsilon_{m'})}} \frac{e^{-\beta \varepsilon_m} - e^{-\beta \varepsilon_{m'}}}{\varepsilon_m - \varepsilon_{m'}} \right] \\ & \times (T_{Al})_{mm'} (T_{Al'})_{m'm}, \end{aligned} \quad (38)$$

where  $\varepsilon_m$  represents the  $m$ th eigenvalue of  $\tilde{\mathcal{H}}_A^t$ . To derive Eq. (31), the conditions  $\langle T_{Ax} \rangle = -\langle T_{Bx} \rangle$ ,  $\langle T_{Az} \rangle = \langle T_{Bz} \rangle$ ,  $Q_{Az} = Q_{Bz}$  and  $Q_{Ax} = -Q_{Bx}$  are used. By using the condition  $\partial \mathcal{F} / \partial \delta T_{\alpha l} = 0$ , the following relations between  $\delta u_l$ 's and  $\delta T_{\alpha l'}$ 's are obtained:

$$\begin{aligned} \delta T_{Ax} + \delta T_{Bx} = & -\frac{4\beta g_0}{D_x} \sqrt{\frac{Vc_0}{N}} \delta u_x \\ & \times \left[ F_{xx} \left\{ 1 - (4J_z^t - 2J_{xy}^t) \beta F_{zz} \right\} + (4J_z^t - 2J_{xy}^t) \beta F_{xz}^2 \right], \end{aligned} \quad (39)$$

$$\delta T_{Az} - \delta T_{Bz} = -\frac{4\beta g_0}{D_x} \sqrt{\frac{Vc_0}{N}} \delta u_x F_{xz}, \quad (40)$$

$$\begin{aligned} \delta T_{Az} + \delta T_{Bz} = & -\frac{4\beta g_0}{D_z} \sqrt{\frac{Vc_0}{N}} \delta u_z \\ & \times \left\{ F_{zz} (1 - 6J_{xy}^t \beta F_{xx}) + 6J_{xy}^t \beta F_{xz}^2 \right\}, \end{aligned} \quad (41)$$

$$\delta T_{Ax} - \delta T_{Bx} = -\frac{4\beta g_0}{D_z} \sqrt{\frac{Vc_0}{N}} \delta u_z F_{xz}, \quad (42)$$

with

$$\begin{aligned} D_x = & (1 - 6J_{xy}^t \beta F_{xx}) \left\{ 1 - (4J_z^t - 2J_{xy}^t) \beta F_{zz} \right\} \\ & - 6J_{xy}^t (4J_z^t - 2J_{xy}^t) \beta^2 F_{xz}^2, \end{aligned} \quad (43)$$

and

$$\begin{aligned} D_z = & (1 + 6J_{xy}^t \beta F_{xx}) \left\{ 1 - (4J_z^t + 2J_{xy}^t) \beta F_{zz} \right\} \\ & + 6J_{xy}^t (4J_z^t + 2J_{xy}^t) \beta^2 F_{xz}^2. \end{aligned} \quad (44)$$

By using Eqs. (39)-(42), the deviation of the free energy from the equilibrium value is given by

$$\mathcal{F} - \tilde{\mathcal{F}}_0 = \frac{1}{2} (c_x(T) \delta u_x^2 + c_z(T) \delta u_z^2). \quad (45)$$

Note that the term proportional to  $\delta u_x \delta u_z$  is absent because of the tetragonal symmetry.  $c_x(T)$  and  $c_z(T)$  are the temperature dependent elastic constants for the  $u_x$  and  $u_z$  modes, respectively. Their explicit forms are given by

$$\begin{aligned} c_x(T) = & \frac{c_0}{D_x} \left[ \left\{ 1 - (6J_{xy}^t - 4g_0^2) \beta F_{xx} \right\} \left\{ 1 - (4J_z^t - 2J_{xy}^t) \beta F_{zz} \right\} \right. \\ & \left. - (6J_{xy}^t - 4g_0^2) (4J_z^t - 2J_{xy}^t) \beta^2 F_{xz}^2 \right], \end{aligned} \quad (46)$$

and

$$\begin{aligned} c_z(T) = & \frac{c_0}{D_z} \left[ (1 + 6J_{xy}^t \beta F_{xx}) \left\{ 1 - (4J_z^t + 2J_{xy}^t - 4g_0^2) \beta F_{zz} \right\} \right. \\ & \left. + 6J_{xy}^t (4J_z^t + 2J_{xy}^t - 4g_0^2) \beta^2 F_{xz}^2 \right]. \end{aligned} \quad (47)$$

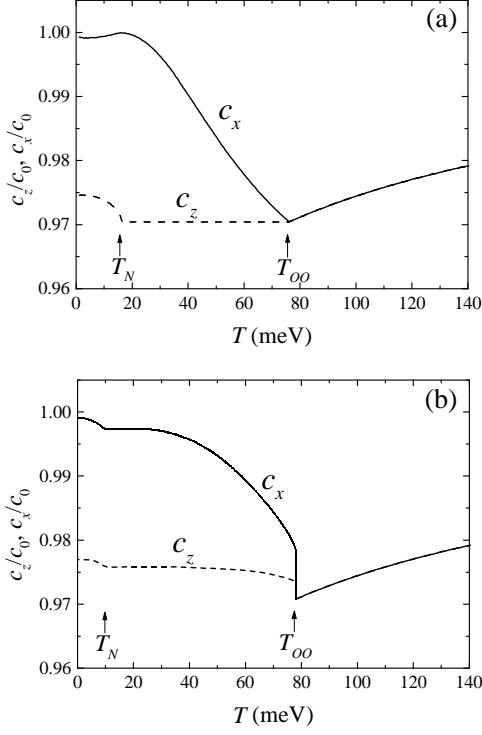


FIG. 4. The elastic constants as functions of  $T$ . Solid and broken curves denote  $c_x$  and  $c_z$ , respectively. Parameter values are chosen to be  $J_1 = 75$  meV,  $J_2 = 25$  meV,  $J_{AF} = 1$  meV,  $ag_{JT} = 6 \times 10^2$  meV,  $a^2K = 17 \times 10^4$  meV and  $a^3c_0 = 2 \times 10^4$  meV. The value of  $B$  is chosen as  $B = 0$  meV in (a) and  $B = 50$  meV in (b).

For  $T > T_{OO}$ ,  $c_x(T)$  and  $c_z(T)$  are simplified as

$$c_x(T) = c_z(T) = c_0 \frac{T + \frac{3}{8}(3J_1 - J_2) + \frac{1}{2}\frac{g_{JT}^2}{K} - g_0^2}{T + \frac{3}{8}(3J_1 - J_2) + \frac{1}{2}\frac{g_{JT}^2}{K}}. \quad (48)$$

The elastic constants are numerically calculated and presented as functions of  $T$  in Fig. 4. Parameter values are chosen to be  $J_1 = 75$  meV,  $J_2 = 25$  meV,  $J_{AF} = 1$  meV,  $ag_{JT} = 6 \times 10^2$  meV,  $a^2K = 17 \times 10^4$  meV and  $a^3c_0 = 2 \times 10^4$  meV. The higher-order JT coupling  $B$  is chosen to be  $B = 0$  meV in Fig. 4 (a) and  $B = 50$  meV in Fig. 4 (b). When  $B$  is comparable to  $J_1$ , the discontinuous change in the elastic constants is found at  $T_{OO}$ . We also obtain a change in  $c_x$  at  $T_N$ . This change reflects the change of the orbital state. As shown in Fig. 5, when  $B$  is much smaller than  $J_1$  (solid curve), the orbital ordered state of the  $\frac{1}{\sqrt{2}}(d_{3z^2-r^2} + d_{x^2-y^2}/d_{3z^2-r^2} - d_{x^2-y^2})$ -type above  $T_N$  changes to the state below  $T_N$  where the component of the  $(d_{y^2-z^2}/d_{z^2-x^2})$ -type increases. On the other hand, when  $B$  is comparable to  $J_1$  (broken curve), the component of the  $\frac{1}{\sqrt{2}}(d_{3z^2-r^2} + d_{x^2-y^2}/d_{3z^2-r^2} - d_{x^2-y^2})$ -type, state increases below  $T_N$ . These changes of the orbital states originate from the spin-orbital coupling in  $\mathcal{H}_J$  in

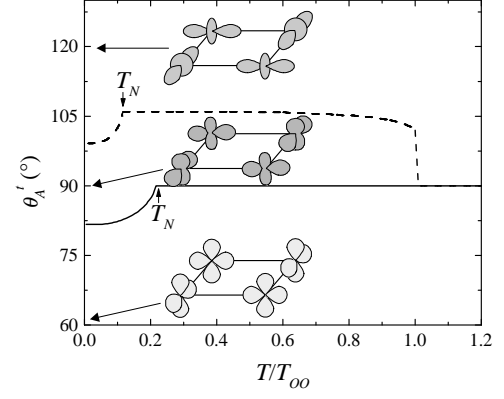


FIG. 5. Temperature dependence of the orbital state.  $\theta_A^t$  is defined by  $\theta_A^t = \tan^{-1}(\langle T_{Ax} \rangle / \langle T_{Az} \rangle)$ . Solid and broken curves are the results for  $B = 0$  meV and  $B = 50$  meV, respectively. Other parameter values are the same as those in Fig. 4. The insets show the schematic orbital structures in the  $xy$  plane.

Eq. (3). The changes of the elastic constants are understood as follows: In the  $\frac{1}{\sqrt{2}}(d_{3z^2-r^2} + d_{x^2-y^2}/d_{3z^2-r^2} - d_{x^2-y^2})$ -type orbital ordered state,  $\langle T_{Ax} \rangle$  is almost saturated as  $|\langle T_{Ax} \rangle| = 1/2$  and  $\langle T_{Az} \rangle = 0$ . Thus, the external strain  $\delta u_x$  does not induce  $\delta T_{Ax}$  and  $c_x$  is saturated. The deviation of the orbital state from the  $\frac{1}{\sqrt{2}}(d_{3z^2-r^2} + d_{x^2-y^2}/d_{3z^2-r^2} - d_{x^2-y^2})$ -type one causes the decrease of  $c_x$  as shown in Fig. 4. This fact reminds us of the inverse of the parallel spin susceptibility  $1/\chi_{\parallel}$  diverging with decreasing  $T$  in an antiferromagnet. We propose that the characteristic change of the elastic constant at  $T_N$  may be used to estimate the coupling constant  $B$ .

## VI. SUMMARY AND DISCUSSION

We have examined the orbital ordering in  $\text{LaMnO}_3$  and the magnitudes of the interactions of the  $e_g$  orbitals between NN sites caused by the virtual exchange of electrons and phonons. By calculating the orbital and spin ordering temperatures and the spin wave dispersion and comparing them with the experimental results, we obtained  $J_1 = 75 \sim 85$  meV,  $J_2 = 25 \sim 40$  meV and  $g_{JT}Q = E_{JT} = 50 \sim 100$  meV.  $E_{JT}$  is much smaller than that in the literature<sup>18,23-31</sup> which was estimated by neglecting the electron-electron interaction. The present results indicate that the orbital ordering in  $\text{LaMnO}_3$  is mainly caused by virtual exchange of electrons under the strong Coulomb interactions.<sup>21</sup> We calculate the temperature dependence of the elastic constants by taking into account both the electron-electron and electron-lattice interactions. It is predicted that the elastic constants show the characteristic change at  $T_N$  which depends on the magnitude of the higher-order JT coupling; when the coupling constant  $B$  is comparable to  $J_1$  (much smaller

than  $J_1$ ),  $c_x$  increases (decreases) with decreasing  $T$ . Through the detailed comparison between theory and experiment, the value of  $B$  may be determined.

The present results support the recent report on the observation of the collective orbital excitation termed orbital wave in  $\text{LaMnO}_3$  by the Raman scattering experiments. Saitoh *et al.* have observed three peak structures around 120-160 meV in the Raman spectra.<sup>39</sup> These peaks can be explained by neither the two-phonon excitations nor the magnetic excitations. The theoretical results of the Raman spectra from the orbital wave agree with the polarization dependence of the spectra and their relative intensities in experiment.<sup>40</sup> Since the characteristic energy of the orbital excitation is much higher than that of the lattice vibration, we introduce the adiabatic approximation for the lattice degree of freedom in the calculation of the orbital wave. Then, the energy of orbital wave is approximately given by  $\omega_{orb} = \sqrt{(3J_1 + \frac{\sqrt{3}}{2}E_{JT})(J_1 + J_2 + \frac{\sqrt{3}}{2}E_{JT})}$ . When we adopt the parameter values obtained in the present analyses  $J_1 = 75$  meV,  $J_2 = 25$  meV and  $E_{JT} = 50$  meV, we obtain  $\omega_{orb} = 187$  meV. These numerical values are consistent with the observed energies of the Raman shifts from the orbital excitations.

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